Assistance Agreement Quarterly Report: 6th Quarter

Date of Report: June 30, 2001

Agreement No: R82806301

Title: **Baltimore Supersite: Highly Time and Size Resolved Concentrations of Urban PM2.5 and its Constituents for Resolution of Sources and Immune Responses**

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Institution: Department of Chemistry and Biochemistry, University of Maryland, College Park, MD

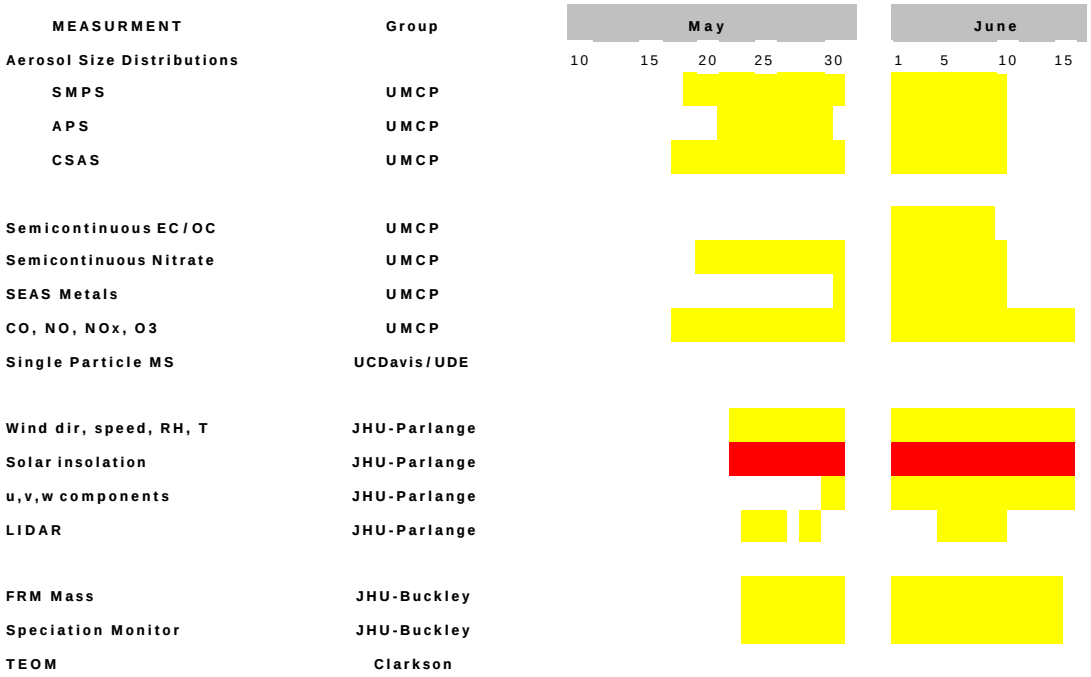
Research Category: Particulate Matter Supersites Program
Project Period: January 15, 2000 to December 31, 2003

Objectives of Research: Our primary objectives are to i) provide an extended, ultra high-quality multivariate data set, with unprecedented temporal resolution, designed to take maximum advantage of advanced new factor analysis and state-of-the-art multivariate statistical techniques; ii) provide important information on the potential for health effects of particles from specific sources and generic types of sources, iii) provide large quantities of well characterized urban PM for retrospective chemical, physical, biologic analyses and toxicological testing, iv) provide sorely needed data on the sources and nature of organic aerosol presently unavailable for the region, v) provide support to existing exposure and epidemiologic studies to achieve enhanced evaluation of health outcome-pollutant and -source relationships, and vi) test the specific hypothesis listed in our proposal.

Status

The Baltimore Supersite trailers were installed at the FMC Corp. site, near Brooklyn and a nominally 20-day intensive sampling program was conducted, beginning in the second week in May and ending on June 10th. As indicated in the figure below, additional measurements were made with some of the instruments until June 15th. The trailers were moved to Clifton Park and installed to temporary power during the last

week in June. Measurements were begun on June 30 with some instruments, however, various problems prevented full operation with all instruments during the July intensive. July and subsequent data will be discussed in the next report.



Progress Summary/Accomplishments

LIDAR/Meteorological Data. The JHU lidar system was deployed at the FMC site during the following days: May: 22, 23, 24, 25, 27, 28; and June: 5, 6, 7, 8, 9, 10, 11, 12, 13, 14. The lidar system could not be operated when it was raining. Data were taken at daytime only in order to comply with FAA regulations. The duration of a lidar scan (vertically pointing upward) was extended from initially 5 minutes to 30 minutes. In some occasions the lidar scans had to be stopped in case of heavy air traffic or because of rain. This extensive data set will provide information on the mixing layer depth, and especially its evolution during the course of the day. In addition, the combination of lidar data, aerosol data and meteorological information could aid in allocating sources of aerosols. The mean wind direction for several periods can be categorized as follows. From 5/28/01 5/31/01 the main wind direction was ranging from 250/-350/. In June for about one third of the days the wind direction was also within this range. Also in June, for one third of the days the mean wind direction was observed to be within 100/-150/. During the remaining days in June, the wind direction was often between 100/-150/ in the morning and in the early afternoon, but was changing frequently at other times of the day. Figure 1 shows and example of a lidar scan, taken on June 14, 2001 at the FMC site (30 minute measurement period, starting at 3:52pm-EST). Higher aerosol concentration can be seen clearly within the atmospheric boundary layer. Figure 2 shows meteorological data from June 14, 2001, where the wind direction is shown on the middle panel.

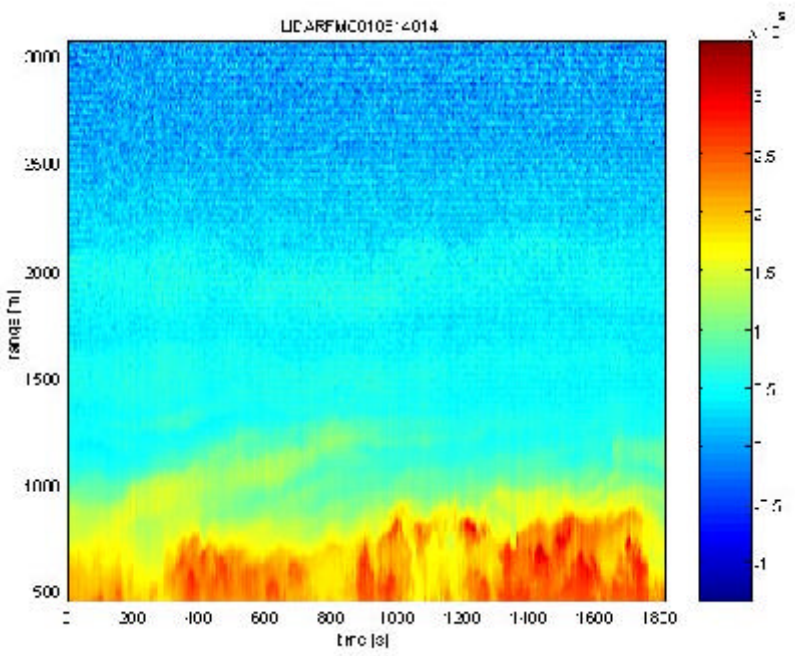


Figure 1. Time-domain scan, showing relative aerosol concentration, taken with the JHU elastic backscatter lidar system during the first intensive measurement period at the FMC site. The relative aerosol concentration increases from blue to red.

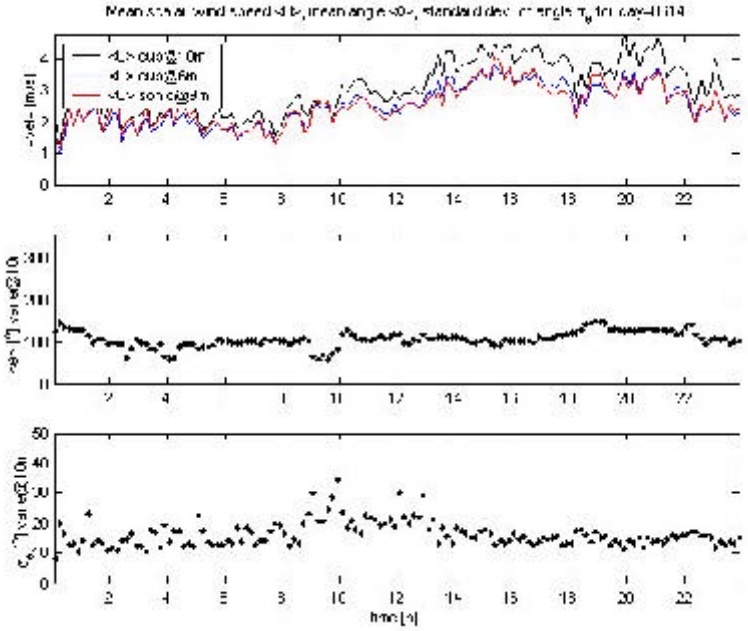
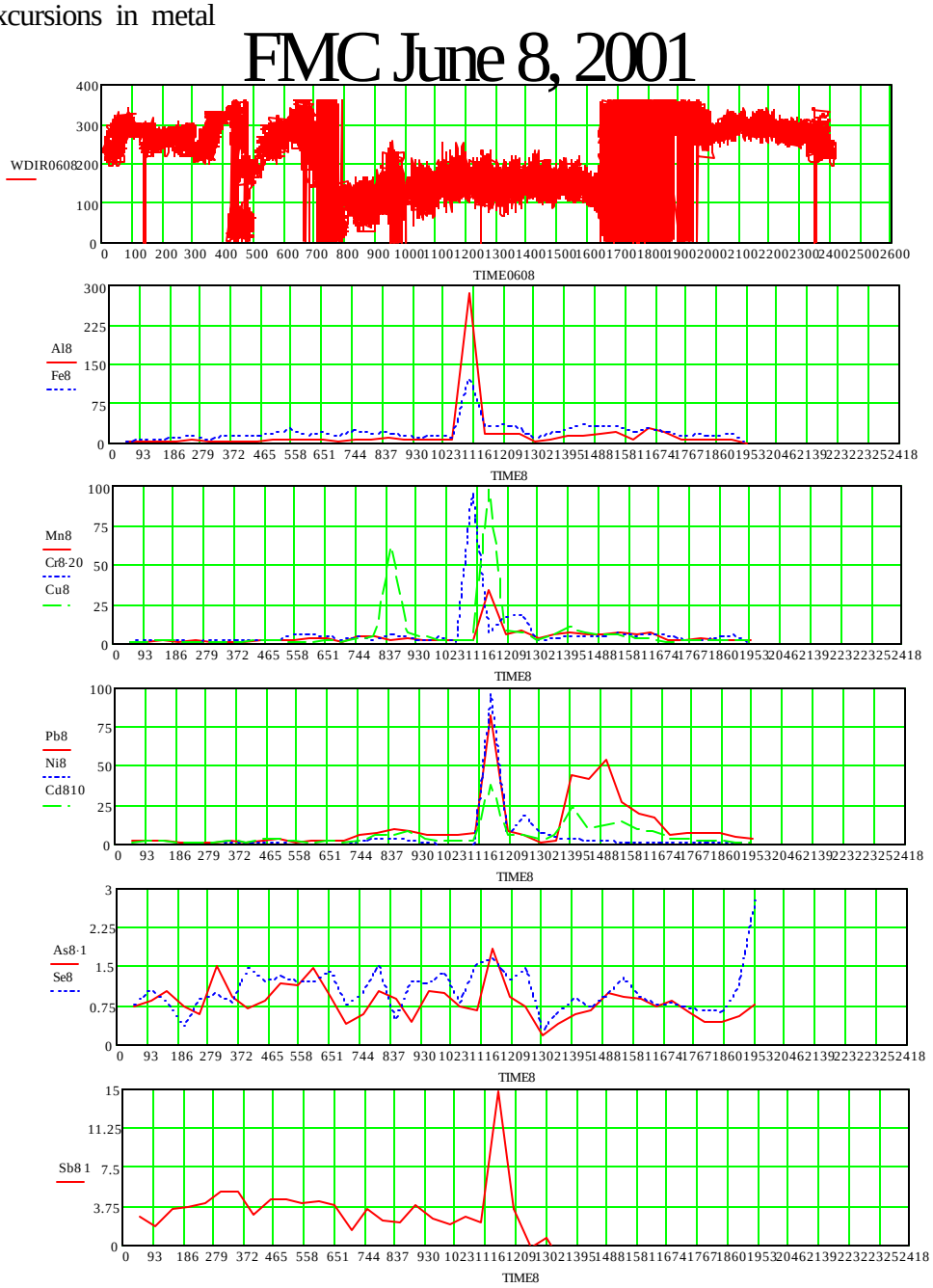


Figure 2. Mean scalar wind speed (upper panel), mean wind direction (middle panel) and the standard deviation of the wind direction (lower panel) on 06/14/2001.

A detailed analysis of the lidar data will furnish the mixing layer height. This information will then be combined with data on aerosol and the meteorological data. Two-dimensional images of relative particle concentration of all data taken during the first intensive measurement period at the FMC site can be found in the lidar data archieve at. http://www.jhu.edu/~dogee/mbp/supersite2001/index.htm

SEAS. A modified SEAS system was installed at FMC and operated in production mode from May 29th until June 10th. Two days worth of samples, collected at sucessive 30 minute intervals were analyzed for 14 elements by Graphite Furnace Atomic Absorption Spectrometry. Preliminary SEAS data for slurry samples collected at FMC on June 7th and 8th show, substantial excursions in metal concentrations during time periods when winds fluctuating winds were from south easterly directions (but not northerly). These are consistent with specific releases from nearby sources, a phenomenon clearly documented by SEAS data collected in St. Louis. The FMC data reveal an interesting dynamic. Concentrations of many metals are typically quite low until there is an event, during which concentrations become elevated by factors ranging from 5 to 100, and then rapidly fall back to back ground levels. This indicates that most of what would be measured by 24-hr integral sampling/analysis methods would be governed by a few relatively brief , but



highly elevated exposures. The signal for Se tends to fluctuate far less. This is likely due the more regional nature of this elements and, hence, its higher background. The Arsenic signal on June 8th appears to be similar in this regard.

Single Particle MS. Construction of the single particle mass spectrometer was completed and the unit was undergoing tests during the month of June.

Cytokine Assays. Studies conducted during the past quarter have established that cultured A549 human lung epithelial cells respond to exposure standard urban particulate matter (NIST 1648 and 1649a particles) by releasing the cytokine IL8. Measurable levels of IL8 were released in a dose response manner over a range of 100 to 250 ug/ml with an exposure time of 24 hr. Air particles <2.5 : m collected by the SEAS instrument as part of this Supersite investigation also stimulated A549 cells to release IL8. A 24 hr sample collected at College Park, MD stimulated cells to release IL8 at calculated *in vitro* particle concentrations as low as 12.5 : g/ml. The response was linear up to a particle concentration of 100 : g/ml. IL8 concentrations in the media ranged from 629 to 5,000 pg/ml. Cells were also exposed to $ZnCl_2$ at concentrations up to 0.5 mM to establish a positive control for this assay. The IL8 response was similar to that observed for the 1648 particles at Zn concentrations of 0.2 to 0.3 mM.

Using this assay system, 10 SEAS samples collected for 30-min intervals were then tested to determine whether short time interval testing could be accomplished. Samples collected at hourly intervals over a 24 hr period at College Park, MD gave rise to quantitatively different responses, with IL8 release ranging from non-detectable < 20 pg/ml to 420 pg/ml. The first set of samples collected from South Baltimore, however, did not stimulate a measurable IL8 response. Metal analyses on these samples will help determine whether these samples were less reactive due to lower metal concentrations.

Cytotoxicity was also measured under the same exposure conditions used for the IL8 studies. The cytotoxic effects of particle exposure were measured using the lactate dehydrogenase (LDH) assay which measures the release of the LDH enzyme from cells resulting from membrane damage. Zn exposure at concentrations up to 0.4 mM did not cause significant cytotoxicity (mean LDH release was 5% at 0.4 mM). LDH release of >20% occurred in response to SM 1648 and 1649a particle exposure, but only at a concentrations of 150 ug/ml and higher. Neither the SEAS samples collected at College Park, nor those collected from South Baltimore, were cytotoxic the to A549 cells over the concentration ranges tested.

Studies have also been initiated to establish whether the RAW264.7 mouse macrophage-like cell line is suitable for use in an assay to determine the ability of particle samples to stimulate the release of cytokines TNF_a and IL6 and the production of reactive oxygen species (ROS) in alveolar macrophage. With the approaches taken thus far, RAW cells do not appear to be responsive to stimulation by particles or LPS. There was no detectable response in the release of the cytokines. Also, production of ROS in response to stimulation by PMA and/or zymogen is minimal; however using increased number of cells it has been possible to measure basal ROS levels using the cytochrome c assay. Work continues using different priming agents.

Organic Compound Sampler. We took delivery of a custom-built sequential organic filter/PUF sampler designed to permit sequential sampling for up to 5 periods at flowrates up to 500 LPM or sequential sampling with 4 channels and simultaneous collection of a 24-hr sample at 100 LPM. However, the Fitler holders and PUF cartridges had to be returned to the vendor for further modifications, as the

hardware engineered to make internal seals was judged to be inadequate. We have now received the re-engineered components, had them industrially degreased or oxygen plasma cleaned (Teflon ball and solenoid valves), and then laboratory cleaned all parts according to a protocol developed by Professor Rogge (distilled water, methylene chloride, followed by acetone rinsing). The support structure provided by the vendor did not allow space to mount the valve actuators, so it was rebuilt on site. The entire system has now been assembled and is (was) ready for testing.

Ultra-High-Volume Aerosol Sampler. A new control program for the system has been developed. The stainless steel 1-m cyclone has been removed and an all-aluminum cyclone has been temporarily installed for pressure drop, flow, and efficiency testing. A new 15-filter cassette box was installed inside the trailer by NIST. The unit has undergone several weeks of testing.

Data base development. We have taken delivery of the data storage computer. The machine was shipped with a RAID 5 array of five 72 GB drives and has an internal capacity of another five 72 GB (or larger) hard drives, permitting a storage capacity of up to 510 GB (total capacity is reduced because of redundancy requirements for RAID 5 configurations). The raid system is handled by a fast, heavily cached, 4-channel controller which can handle two additional external raid arrays if needed. Total capacity of the raid system is at least 16 drives per channel. We intend to store all of the supersite raw data, including all QA/QC and diagnostic data from the instruments, with the possible exceptions of LIDAR and Single Particle MS data. The database has been created and tables for data from the following instrument types have been defined:

* 3D Sonic Anemometer
* APS
* CPC (May need work, based on initial file info.)
* CSAS
* Gases (CO, NO2, NOX, O3, SO2)
* Nitrate
* SEAS
* SMPS
* SPMS (May need work - based on initial file info.)

Import routines completed for the SEAS, Forward Scattering laser spectrometer, Nitrate Monitor, Sulfate monitor, gases, SMPS, and FMC met data (there have been some format and instrument changes). The import routines are now being verified for proper execution and project data will be loaded from the raw data archive to the database shortly.

Website: Our Static Web site (www.chem.umd.edu/supersite) contains color maps of the Baltimore Region have been prepared in ARCVIEW and loaded onto our website. The maps show major PM emission sources (obtained from the EPA AIRS data base), metals emission sources (TRI data), and estimates of emissions as well as the location of our sampling sites and key streets. Recently, we've added a site plan for the supersite at Clifton Park; our position papers on the RH issue and allocation of intensive resources; the efficiency curve for the UMCP all glass inlet impactor; SEAS data taken at College Park, MD, showing resolution of sources; and a 2-D scan showing relative particle concentration data showing

traffic pollution over Baltimore streets. Current versions of all SOPs are now available on the web site.

Personnel Changes. Dr. Yu-Chen Chang joined the UMCP Supersite Team on January 16th, 2001. Doctoral student, Dawn Catino, joined our group on February 10th. Ms. Catino's work will encompass RDI/sychrotron XRF measurements.

Publications/Presentations/meetings: No publications have yet been prepared. Two papers are planned for presentation.

AAAR, 2001: Source Identification by a Multilinear Receptor Model Using Highly Time Resolved Chemical Composition and Wind Data, XIN-HUA SONG, Clarkson Univ, Philip K. Hopke, Clarkson Univ, Pentti Paatero, Univ of Helsinki, John M. Ondov, Univ of Maryland, Christopher B. Kidwell, Univ of Maryland

In Vitro Assay of the Biological Activity of Ambient $PM_{2.5}$ Collected By A High Frequency Aerosol Sampler. R Mitkus[1], M Falconer[1], J Powell[1], J Ondov[2], K Squibb[1], University of Maryland, Baltimore, MD and [2]University of Maryland, College Park, MD

Future Activities:

1. We will continue to hold weekly PI teleconferences as needed
2. Additional SEAS samples are being selected for for cytokine assay testing.
3. FMC data are being quality assured and entered into the data base.
4. Various observations and inferences will be discussed during the Supersites meeting at RTP in November.

Supplemental Keywords: Single Particle Mass Spectrometry, ROS, Cytokine, Receptor Modeling

Met Data Progress Report
for time: II/2001

05/26 deployment of sensors and erection of tower
05/27, 9am start of measurements
instruments: rain gage sampled at 1 Hz
Vaisala hygrometer and temperature sensor at 4.75m and 1Hz
2 Cup anemometers at 5.7m and 10.24m and 1 Hz
wind vane at 10.24m at 1 Hz
measured variables: relative humidity (RH), Temperature in degrees Celsius, length of horizontal wind vector in m/s, wind direction in degrees
derived variables: standard deviation of wind direction, mean horizontal wind velocity (vector and scalar method)

05/30 additional instrument: 3 dimensional campbell scientific sonic anemometer (CSAT3 3-D Sonic Anemometer)
additional measured variables: all three components of wind vector in m/s at 8.94m sampled at 10 Hz, virtual potential temperature in degrees Celsius at 10 Hz
additional derived variables: 10 min averages of (col 4-14 in ave files): air temperature [^o C], relative humidity [%], velocity for first cup (scalar and vector mean) [m/s], velocity for the second cup (scalar mean) [m/s], horizontal wind direction [^o], std deviation of horizontal wind direction [^o], rain (sum over 10 min) [mm], friction velocity u* [m/s], Obukhov length L [m], sensible heat flux H [J/m^2s]

06/15 14h end of measurements at FMC

missing values for duration of >1 hour:
05/30 20h-22h all instruments
06/04 12h - 06/05 16h all instruments

data quality
all sensors functioned properly during all times, intercomparison of data from 3d sonic anemometer with cup anemometers and vaisala temperature probe assures data quality

completeness (during 5/27 - 6/15):
30 hours missing out of 457 --> 93% complete

data presentation
all data is available as graphs at
http://www.jhu.edu/~dogee/mbp/index.html
raw data files and averaged statistics are backuped on DVD and stored on FATBOY

Lidar Data Progress Report
for time: II/2001

05/22 start of the measurements
measurement days:
May: 22, 23, 24, 25, 27, 28; June: 5, 6, 7, 8, 9, 10, 11, 12, 13, 14.

type of data
vertical scan at a wavelength of 1064 nm with a duration of 5, 15 or 30 min.

data presentation
raw data files are backuped in DVD and stored on FATBOY

All plots, with background substration and range correction are available at
http://www.jhu.edu/~dogee/mbp/supersite2001/lidar_data.htm